EFFECT OF SOIL HEAVY METAL CONTAMINATION UPON GROWTH AND NUTRIENT COMPOSITION OF CORN

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ABSTRACT

EFFECT OF SOIL HEAVY METAL CONTAMINATION UPON GROWTH AND NUTRIENT COMPOSITION OF CORN

By

Richard Henry Leep

A greenhouse study was conducted using a Houghton muck (pH 6.7), treated with $CdCl_2$, $CrCl_3$, $NiCl_2$ and $ZnCl_2$ and cropped with corn.

Cadmium and Cr were applied in equal milliequivalent concentrations ranging from 0.05 to 2.0 milliequivalents of metal/100 g soil. Nickel and Zn applications ranged from 0.1 to 9.0 milliequivalents metal/100 g soil. Treatments were replicated four times and a control set was included. After harvest, corn plants and soil samples were analyzed for Cd, Cr, Cu, Fe, Mn, Ni, and Zn by atomic absorption spectrophotometry. Plant samples were analyzed for Ca, K, Mg, and P by emission spectroscopy.

Plant growth and heavy metal uptake was influenced quite differently by Cd, Cr, Ni, and Zn. Additions of Cd caused delayed seedling emergence, stunting of plants, and plant dry weight reduction. Cadmium accumulation in plant tissue increased significantly with graded additions of Cd.

Plants grown on Cr treated soil yielded significantly higher in dry weight compared to the control. However, a subsequent chemical analysis of plant tissue revealed no detectable Cr. Significantly higher levels of Mn were detected in the plant.

Graded additions of Ni up to 3.0 meq/100 g increased plant growth significantly over the control. Rates of Ni above 3.0 meq/100 g reduced plant growth significantly indicating a probable Ni toxicity. The plants accumulated Ni in relatively high amounts.

Plant size was similar to the control on all Zn treatments. Zinc accumulation in plant tissue up to 1763 ppm indicates that Zn was readily available for plant uptake.

The soil extractants varied greatly in their ability to extract metals from the soil. Both 0.1 $\underline{N}$ HCl and 0.005 $\underline{M}$ DTPA worked well in extracting heavy metals and were about equal in amounts extracted. 1 $\underline{N}$ NH_4OAc was somewhat less effective than 0.1 $\underline{N}$ HCl and 0.005 $\underline{M}$ DTPA in terms of amount of metal extracted, however, each extractant removed increasing amounts of metals corresponding to graded additions of metals with the exception of Cr additions in which only 0.1 $\underline{N}$ HCl removed Cr.

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INTRODUCTION

The public is becoming increasingly concerned with the pressing problems of municipal or industrial waste disposal and possible entry of toxic materials into waterways. This concern has prompted municipalities, government agencies, and universities to investigate alternative methods of disposal. One alternative method which has received much attention is land disposal or the spreading of urban wastes onto agricultural land.

The practice of spreading wastes onto land has been used for many years on a limited scale. Much of the research on the use of sludges or wastes for agricultural land has been concerned with the fertilizing value of the materials. However, many sludges or wastes contain substantial quantities of heavy metals (Cd, Cr, Cu, Ni, and Zn) which are toxic to living organisms.

Cadmium in all its chemical forms is toxic to living species (Fulkerson and Goeller, 1973). Plants grown on soil amended with Ni resulted in severe plant toxicities and growth retardation (Crooke, 1955; Traynor, 1974; Vanselow, 1966). Chromium has been seen to be toxic to many species of plants (Pratt, 1966; Soan and Saunder, 1959; Schueneman and Ellis, 1973). Zinc is considered an essential element for plant growth, however, excessive accumulation of Zn can cause a Zn toxicity (Melton, 1968).

The extent to which heavy metals are inactivated for plant uptake may vary greatly from soil to soil, depending upon cation exchange capacity, percent organic matter, clay content, and pH (Haghiri, 1974; John, 1972; Traynor, 1974).

Heavy metals contained in many sewage sludges are potentially toxic to plants. This study was initiated to evaluate effects of graded additions of Cd, Cr, Ni and Zn on grown of corn plants on a Houghton muck soil. Yields of dry matter, and metal and nutrient contents of the plants, were determined. The extraction behavior of selected metals was studied to throw some light on mechanisms for their inactivation in soil.

REVIEW OF LITERATURE

Cadmium in Soil

Lagerwerff (1972) discussed the presence of Cd in the soil. He has found that the presence of Cd is normally linked to that of Zn because of their geochemical kinship and incomplete technical separation. Parent rock materials of basaltic origin have a higher concentration of Cd than those of granite rocks (Traynor, 1974).

Total concentrations of Cd typically found in soils average 0.06 ug Cd/g soil with a range of 0.01 to 7.0 ug Cd/g soil (Allaway, 1968).

Cadmium may reach the soil as an aerosol constituent, through precipitation or direct deposition. Direct deposition may occur near factories or mines handling Zn. Cadmium is also deposited in soils as an impurity in phosphate fertilizers, or as a constituent of certain fungicides which are sprayed onto crops (Lagerwerff, 1972). Cadmium in roadside plants and soils, decreasing with distance from the traffic, was attributed to Cd as an impurity in Zn containing additives in motor oils and Zn compounds used in vulcanization of rubber tires (Lagerwerff and Specht, 1970). Sewage sludges used in land waste disposal may contain relatively high amounts of Cd, depending on the area or location the sludge comes from.

John (1972) has described Langmuir adsorption isotherms for 30 soils from British Columbia. He determined the adsorption maximum and a coefficient relating to the bonding energy of the soil for Cd. The adsorption maxima for all soils were similar in magnitude and correlated with Al and Zn soluble in 0.01 M $CaCl_2$. The coefficient related to the bonding energy generally decreased in the order: organic> heavy clay>sandy and silt loam>sandy soils.

Ellis and Knezek (1972) have reviewed literature pertaining to relationships of various metals and soil organic matter as well as known and proposed mechanisms by which metals are adsorbed by organic matter.

Stability diagrams for chelates of Cd^{++} have been presented by Norvell (1972) to illustrate one method of estimating the influence of chelating agents on the solubility of potentially hazardous heavy metals in soils. The effectiveness of eleven chelating agents for Cd^{++} in calcareous soils would be in the order: DTPA>CDTA, EDTA>HEDTA, EGTA>NTA>P_2O_7, P_3O_{10}, CIT>OX>EDDHA (diethylenetriaminepentaacetic acid, cyclohexanediaminetetraacetic acid, ethylenediaminetetraacetic acid, hydroxyethylethylenediaminetriacetic acid, ethyleneglycol-bis (2-aminoethylether) tetraacetic acid, nitrolotriacetic acid, pyrophosphoric acid, triphosphoric acid, citric acid, oxalic acid, ethylenediamine di-*o*-hydroxyphenylacetic acid, respectively). Cadmium chelates such as Cd-DTPA (at high pH) or Cd-EGTA (at low pH) would be effective in increasing Cd solubility.

DTPA (0.005 M) was used as an effective soil extractant for extraction of Cd from Rubicon sand and a Morley clay loam (Traynor, 1974).

Role of Cadmium in Plants

Cadmium is not considered an essential element for plant growth. Studies of plants grown on soils containing excessive amounts of Cd indicate that Cd is absorbed very readily. Haghiri (1973a) demonstrated that foliar-applied Cd was readily translocated into various parts of soybeans, however, uptake of Cd via the root system was significantly higher. Cadmium in various parts of the soybean plant decreased in the following order: stem>leaves>pods>beans.

John, Chuah, and VanLaernover (1972) grew oats on a soil contaminated with Cd deriving from a battery smelter in British Columbia. They reported very high Cd accumulations in the roots, but much smaller amounts of Cd in the shoots.

John (1973) studied Cd uptake by eight food crops as influenced by various soil levels of Cd. He found that certain crops accumulate excessive amounts of Cd from soil treated with Cd from inorganic sources. Plant species vary greatly in their ability to accumulate Cd from both soil and nutrient culture solutions (Haghiri, 1973b; Yamagata and Shigematsu, 1970; Turner, 1973; Page, Bingham, and Nelson, 1972).

Bingham et al. (1973) grew corn, wheat, rice, field beans, soybean, cabbage, spinach, turnip, radish, tobacco, tomato, and squash, to commercial harvest stage using a soil pretreated with a municipal sludge (1%) containing variable amounts of $CdSO_4$. Sensitive plants such as soybean, spinach, and field beans were injured by soil additions as low as 10 to 20 mg Cd per kg of soil. Cabbage, tomato, and rice tolerated 400 to 600 mg Cd per kg soil.

Preliminary work by Allaway (1968) indicated that plant growth depression due to Cd toxicity tended to occur after plants had accumulated approximately 3 ppm of this metal. Normal concentrations of Cd in plants were reported to fall in a range of 0.2 to 0.8 ug/g of dry plant material.

Fulkerson and Goeller (1973) report that Cd may replace Zn as a cofactor and thereby cause many Zn-related enzymes to be non-functional. Symptoms of Cd poisoning may mimic a Zn deficiency.

Traynor (1974) reported Cd toxicity in corn causing a severe growth retardation. John, VanLaernover, and Chuah (1972) in a study of factors affecting plant uptake and phytotoxicity of Cd added to soils, reported reduced yields of radishes showing chlorosis by soil application of 100 ppm Cd. He correlated Cd uptake with a variety of soil variables. The ability of soils to absorb Cd was inversely proportional to Cd uptake. The same relationship applied to Cd absorption in high soils. Cd was more available to plants on acid soils.

Lagerwerff (1971) found that increasing soil pH by liming somewhat supressed plant Cd uptake. Bremer and Baker (1973) conducted greenhouse experiments on a soil known to contain excessive levels of soil Zn and Cd. Treatments of $CaCO_3$ and $MgCO_3$ which increased soil pH gave better yields and somewhat suppressed plant Cd concentration.

Lagerwerff and Biersdorff (1972) studied the interaction of Zn with uptake and translocation of Cd. Cadmium was added to a complete nutrient solution at 2, 20, and 100 ppb and factorially combined with 20, 100, and 400 ppb Zn. The two largest levels of Cd and Zn suppressed the uptake of Cd into the roots and leaves. However, at the highest concentration of Cd and Zn, there was an increase in Cd uptake. Zinc may have been somewhat toxic at the 400 ppb level.

Haghiri (1974) studied the effects of several soil factors upon Cd uptake by plants. Cadmium concentration in oat shoots was decreased by increasing the cation exchange capacity (CEC) of the soil. Except for its CEC effect, organic matter did not influence Cd uptake in oat shoots. These results indicate the retaining power of organic matter for Cd may be predominantly through its CEC property rather than its chelating ability. Cadmium concentration in oat shoots was increased with increasing soil temperature.

Chromium in Soil

Chromium is widely distributed in soil, water, and biological materials (Pratt, 1966). Concentrations of Cr commonly found in soils range from 5 to 3000 ug/g of soil, with an average of 100 ug/g soil (Allaway, 1968). Soils derived from ultra-basic or serpentine rocks, called serpentine soils, may have concentrations of Cr up to several percent (Pratt, 1966). Chromium is found in sewage sludges in varying amounts, depending upon location or source of the sludges (Peterson, Lue-Hing, and Zenz, 1973).

The most stable oxidation state of Cr is the trivalent state, although Cr can occur in each of the oxidation states from -2 to +6. In the trivalent state, Cr has a strong tendency to form coordination compounds, complexes, and chelates (Mertz, 1969).

Organic matter adsorption reactions with Cr may be important in controlling available Cr in soil solution. Stevenson and Ardakani (1972) in a review on organic matter reactions involving micronutrients in soils, indicated that humic and fulvic acids can bind metal ions through both electrostatic forces (attraction of a positively charged metal ion to an ionized COOH group) and by electron pair sharing (formation of covalent linkage).

Fulvic acids were found to form at least four types of chelate with Cr (Stevenson and Ardakani, 1972).

Sorption and desorption of heavy metals by hydrous oxides of Fe and Mn may be important in controlling their availability. Jenne (1968) proposed that the hydrous oxides of Mn and Fe, which are nearly ubiquitous in clays, soils, and sediments, are principle agents in the fixation of heavy metals in soils and fresh water sediments. Results of an experiment conducted by Tiller et al. (1963) indicate that fixation of heavy metals is related to the presence of adequate amounts of hydrous Fe and Mn oxides in the soil.

Role of Chromium in Plants

Mertz (1969) has reviewed literature on the occurrence and function of Cr and has noted a number of beneficial effects upon plants and animals. However, specific functions of Cr in plants have not been determined, and existing knowledge of its role in vegetation is far from complete. Pratt (1966) indicated some of the beneficial effects of added Cr salts may have resulted from response to elements added with Cr, or to indirect effects.

Tiffin (1972) found three anionic Cr complexes in extracts of manuka tea-tree. The xylem sap contained only $Cr_2O_4^{-2}$ ions.

Many researchers have studied toxic effects of Cr upon plants grown in both nutrient solutions and in the soil. Hunter and Vergnano (1953) found that the growth of oat plants was 32, 30, 25, 22, 19 and 13 cm, respectively, with 0, 5, 10, 15, 25 and 50 ppm of Cr as potassium chromate added to nutrient solutions. At 5 and 10 ppm, the effect was one of chlorosis. At 15, 25, and 50 ppm, specific symptoms of Cr toxicity appeared: stunting, with narrow, brownish-red leaves containing small necrotic areas and poorly developed roots.

Hunter and Vergnano (1953) were of the opinion that the principle accumulation and toxic effect of Cr occurred in the roots of oat plants. Soane and Saunder (1959) reported that the Cr content of tobacco roots were 20 times the content of the leaves of plants showing Cr toxicity. The leaves of the plants showing Cr toxicity had only slightly higher Cr content than leaves from healthy plants.

Specific Cr toxicity symptoms for corn plants were reported by Soane and Saunder (1959). The toxicity range for Cr in corn leaves ranged from 4 to 8 ppm. The plants were severely stunted, while the leaves had a tendency to roll around the shoot. The leaves were purple-green and narrow, with intense purple color on the lower 2 inches of the lower blades.

Cropper (1967) reported Cr toxicity symptoms of corn similar to those reported by Soane and Saunder (1959). In an experiment in which corn was grown on a silt loam and a sandy soil containing sewage sludge with increasing amounts of Cr, Cropper (1967) found decreased Fe, P, and Zn uptake at the highest rate of applied Cr. Manganese content was increased twice over the control. The plant Cr concentration was lower on the silt loam soil as compared to the sandy soil. This may be due to the increased cation exchange capacity or organic matter in the silt loam soil complexing Cr and subsequently making it less available to the plant.

Schueneman and Ellis (1973) reported that plant response to added soil Cr varied with organic matter in the soils studied. Plant growth was stimulated by application of 50 ppm Cr^{+3} on a soil containing high organic matter while the 50 ppm rate of Cr^{+3} on a soil low in organic matter decreased plant growth.

Schimp et al. (1957) and Prince (1957a, 1957b) report normal concentrations of Cr in corn tissue as follows: leaves of young corn plants ranged from 0.74 to 2.07 ppm Cr. Leaves at tasseling stage ranged from 0.69 to 1.22 ppm Cr. Leaves of mature plants ranged from 0.44 to 0.80 ppm Cr. Stalks of mature plants contain an average of 0.22 ppm Cr.

Nickel in Soil

Vanselow (1966) states that soils normally contain from 5 to 500 ppm of Ni, with an average of 100 ppm. Soils derived from sandstone, limestones, or acid igneous rocks generally contain less than 50 ppm Ni, while those soils derived from igneous rocks may contain from 5 to 500 ppm Ni. In a few areas, soils derived from unltrabasic igneous rocks could contain as much as 2000 ppm of total Ni (Hodgson et al., 1966).

Exchangeable Ni, as determined by 1 $\underline{N}$ NH_4OAc rather than total Ni in soils, appears to be closely correlated with the availability of Ni to plants (Soane and Saunder, 1959). Traynor (1974) has noted that Ni occurs in nature mainly in combination with As, At, and S. Only NI^{+2} occurs in the ordinary chemistry of the element.

Results of research by Schnitzer and Skinner (1966, 1967) indicated the following order of stabilities of complexes found between a soil fulvic acid and nine divalent cations: Cu>Fe>Ni>Pb>Co>Ca>Zn>Mn>Mg at pH 3.5. When the pH was raised to pH 5.0, the order was changed to: Cu>Pb>Fe>Ni>Mn>Co>Ca>Zn>Mg.

Ellis and Knezek (1972) have noted that organic complex formation with metals through chelation or sequestration is an important bonding mechanism in soils.

Stability diagrams for chelates of Ni^{++} have been presented by Norvell (1972) to illustrate one method of estimating the influence of chelating agents on the solubility of potentially hazardous heavy metals in soils. The effectiveness of chelating agents as chelates for Ni^{+2} in calcareous soils would be in order: DTPA, HEDTA, EDTA>CDTA>NTA>EDDHA>CIT>OX, EGTA, P_3O_{10}. Clearly, DTPA, HEDTA, EDTA, and CDTA could most effectively increase the solubility of Ni^{+2} in soils.

Traynor (1974) using Langmuir adsorption data, has indicated that much of the Ni added to soil was inactivated through an adsorption mechanism.

Crooke (1956) showed that toxic effects of serpentine soils high in Ni can be greatly alleviated by liming the soil, resulting in reduced availability of Ni.

Massey (1972) conducted a study of soil contaminated from mining operations in Kentucky. Of the 3 metals studied, Cu, Zn, and Ni, nickel is the most likely to remain in solution in toxic amounts after the soil pH is raised by liming. Approximately 4.3, 2.5, and 1.4 ppm Ni was left in solution at pH 4.5, 5.5, and 6.5, respectively.

Traynor (1974) has noted that hydrous oxides of Mn and Fe which are nearly ubiquitous in clays, soils and sediment, may exert the principal control on the fixation of Co, Ni, Cu and Zn.

Role of Nickel in Plants

Nickel is not considered as essential element for plants. Experiments by Tiffin (1972) have revealed negatively charged Ni in xylem exudates of tomato, cucumber, corn, carrot, and peanut. Schroeder et al. (1967) stated that Ni behaves similar to an essential trace element. Traynor (1974) indicated Ni activates several enzymes including arginase, carboxylase, acetyl coenzyme A synthetase, and trypsin. It was also noted that Ni inhibits acid phosphatase under certain conditions and catalyzes the enzymatic decarboxylation of oxalic acid.

Cropper (1967) investigated the effect of added soil Ni to a sludge-amended soil. He found that Ni accentuated a Ca deficiency symptom observed in the control. Potassium, Mn, and Zn uptake was increased by increasing soil Ni levels. Crooke and Inkson (1955) noted that the concentration of Ca in dry matter of the plant tops was more than doubled in the presence of Ni toxic tissue.

Vanselow (1966) and Crooke and Knight (1955) have described symptoms of oat plants affected by Ni toxicity as a deficiency of plant metabolism causing white necrotic striping of the leaves accompanied by an induced Fe deficiency chlorosis.

Crooke, Hunter and Vergnano (1954) studied the relationship between Ni toxicity and Fe supply and found that an increase in the Fe level in the nutrient solution produced a reduction in Ni toxicity symptoms and Ni content in oats. In further experiments Crooke and Knight (1955) and Crooke (1955), using autoradiographs of leaves and plants supplied with radioactive Fe, showed that necrotic areas in the leaf matched areas of low Fe content. They suggested there was a migration of nutrients out of the dying tissue. These experiments also indicated that a high Fe supply reduced the severity of necrosis no more than could be accounted for by the reduction in Ni content.

An experiment conducted by Hunter and Vergnano (1952) indicated a wide range of crops vary considerably in their susceptibility of Ni toxicity. Many crops were tested and their resistance to toxicity of Ni from greatest to least are listed in the following order: barley>wheat, ryegrass, beans>oats, clover, potatoes>turnips, swedes, cabbage, kale>beets.

Allaway (1968) indicated that normal levels of Ni in plant tissue were about 1 ug/g plant tissue while a toxic level would be anything greater than 50 ug/g plant tissue.

Zinc in Soil

Krauskopf (1972) reports concentrations of Zn in igneous rocks of basaltic origin and granite origin as 100 ppm and 40 ppm, respectively. Among ordinary sedimentary rocks the greatest concentrations of Zn are found in shales.

The chemistry of Zn shows only a single valence state in natural materials. A weathering of Zn minerals gives Zn^{+2} in solution.

The total Zn content of soils varies from 10 to 300 ppm (Allaway, 1968). In most soils, more Zn is found in the surface that in subsurface horizons (Chapman, 1966).

Bould (1963) stated that Zn is adsorbed as a divalent cation on clays or complexed by organic matter after release from the minerals. Bingham, Page, and Sims, (1964) reported that montmorillonite is capable of adsorbing Zn or Cu beyond its cation exchange capacity, particularly at near-neutral or alkaline pH levels. This was explained as a result of precipitation of Zn as $Zn(OH)_2$. Jurinak and Thorne (1955) stated that chemical complexes, strong clay adsorption complexes and Zn hydroxide were formed in soils.

Ellis and Knezek (1972) and Stevenson and Ardakani (1972) have reviewed literature related to relationships between Zn and soil organic matter and proposed mechanisms by which Zn is adsorbed by organic matter. Soil organic matter forms very stable complexes with both Zn and Cu. Himes and Barber (1957) removed organic matter from soil and destroyed the chelating ability of the carboxyl and phenolic functional groups. Randhawa and Broadbent (1965) showed that the complexing ability of humic acid increased rapidly with an increasing hydroxyl ion concentration up to pH 8.5.

Hodgson, Lindsay and Trierweiler (1966) found that only a small proportion of total Zn in the soil is complexed by organic matter. However, 28 to 99 percent of the Zn in soil solution is complexed by organic matter.

Norvell (1972) calculated ratios of chelated Zn to Zn^{+2} for 11 chelating agents. In the pH range of calcareous soils their effectiveness as Zn^{+2} chelates are in the order: DTPA>CDTA,HEDTA, EDTA, NTA>EGTA>CIT, EDDHA, P_3O_{10},P_2O_7, OX. The degree of chelation of Zn^{+2} by EGTA, CIT, EDDHA, P_3O_{10}, P_2O_7, and OX is similar to that for natural complexes of Zn^{+2} in soil solution.

Role of Zinc in Plants

Chapman (1966) noted that the essentiality of Zn for plant life was not fully accepted until the early 1930's. Bonner and Varner (1965) indicated a concentration of approximately 20 ppm Zn in plant tops appeared to be optimal for normal plant growth and metabolism. Allaway (1968) reports that a normal concentration of Zn found in plants range from 15 to 200 ug/g plant tissue while a toxic range may be greater than 200 ug/g plant tissue.

Melton, Ellis and Doll (1970) conducted an experiment in which 3 levels of Zn were added to 20 Michigan soils and pea beans were grown. Pea bean growth was reduced by both

Zn deficiency (below 20 ppm) and toxicity (above 50 ppm Zn in plant tissue).

Chapman (1966) found levels of Zn in plant dry matter ranging from 20 ppm to 10,200 ppm. Clearly, Zn may readily accumulate in plants in considerable amounts.

The primary role of Zn in plant growth is that of a catalyst. Prince, Clark and Funkhouser (1972) noted that Zn is an essential component of a variety of dehydrogenases, proteinases, and peptidases. Zinc may be involved in chlorophyll synthesis and rate of transpiration (Schutte, 1964).

Visual deficiency symptoms in plant tops are interveinal chlorosis, necrosis of lower leaves, and shortening of internodes (Melton, 1968). Zinc toxicity symptoms for corn was described by Cropper (1967) as stunting, lower yields, and bright red older leaves. Chapman, Liebig and Vanselow (1940) produced Fe chlorosis in citrus grown on sand and solution cultures containing excessive Zn. Iron chlorosis was produced in oats grown in sand culture with added increments of Zn up to 100 ppm. At 25 ppm of added Zn, the chlorosis was faint and the leaves contained 1,700 ppm Zn. When 100 ppm was added, the chlorosis became more severe with the leaves accumulating 7,500 ppm Zn (Hunter and Vergnano, 1953).

King and Morris (1972) reported a decrease in soil pH with sewage sludge treatments with a resultant increase in exchangeable and water-soluble Mn and exchangeable Zn in the soil. Terman, Soileau and Allen (1973) conducted an experiment to study the possible toxic effects of Zn buildup in an acid soil from heavy application of a Johnson City compost. Concentrations of Zn in plant tops was increased. However, liming the soil reduced plant Zn concentration and toxicity.

Bremer and Baker (1973), Chaney (1973), and Melton et al. (1970) have observed that plant Zn uptake is dependent upon soil pH and texture. Rogers and Wu (1948) concluded that liming reduced Zn uptake by increasing soil pH. Bingham and Garber (1960) related soil type to P-induced Zn deficiency. A reduction in both P and Zn uptake was found in kidney beans, corn, and tomatoes when P was applied to limed soils (Burlson, Dacus and Gerard, 1961; Ward et al., 1963). Heavy P application generally induced greater Zn deficiency on soils above pH 7.0 (Melton et al. 1970).

EXPERIMENTAL METHODS

Greenhouse Studies

The effect of heavy metal contaminants on growth and mineral composition of corn was evaluated in the greenhouse using a Houghton muck soil supplied with increasing additions of Cd, Cr, Ni and Zn. Rates of application were based, in part, on existing information regarding toxicities of these metals and, in part, on visual observations of plant response in a pilot study.

Seven levels of addition were used. For Cd and Cr, these were 0.05, 0.1, 0.25, 0.5, 0.75, 1.0 and 2.0 meq/100 g. Additions of Ni and Zn were 0.1, 0.2, 0.5, 1.0, 3.0, 6.0 and 9.0 meq/100 g. The metals were supplied as the chloride salts and mixed thoroughly with the soil two weeks prior to planting. A control treatment did not receive any of these metals but was otherwise handled similarly.

Uniform additions of Mn, N, P and K were incorporated with each experimental lot of soil. The Mn addition was 20 ppm as manganese sulfate. Nitrogen, P and K were added as recommended for corn by the Michigan Cooperative Extension Soil Testing Lab (N-P-K = 150-100-50 kg/ha).

Prior to these amendments, the Houghton muck had been passed through a 6-mesh stainless steel screen and mixed thoroughly. After treatment, the soil was dispensed in 3-quart plastic pails which were used as growth containers (1.4 kg per container). Quadruplicate containers were set up for each of the 29 treatments and were arranged as randomized blocks in the greenhouse.

On April 25, 1973, ten corn seeds (variety Michigan 500) were evenly spaced three-fourths inch below the soil surface and 1.5 inches from the edge of each container. All containers were watered with 100 ml of deionized water after planting. After seed germination, deionized water was added daily as needed, each container being brought up to a constant weight twice weekly. Three hours of supplemental lighting was used daily.

Plants were thinned to six per container two weeks after germination. Plastic stakes were inserted into the pots to support the plants. Plant growth differences were recorded with photographs.

On May 30, 1973, plant tops were cut with stainless steel razor blades and dried at 60°C in paper bags. Dry weights were recorded. A stainless steel Wiley mill was used to grind the plant samples to pass a 20 mesh screen.

Plant Analytical Methods

One gram portions of the dry ground plant samples were wet ashed with nitric and perchloric acids in 100 ml Kjeldahl flasks. The reduced volume (5 ml) was brought up to 100 ml with deionized water and Cd, Cr, Cu, Fe, Mn, Ni, and Zn content of the digest was analyzed with a Perkin-Elmer 303 atomic absorption spectrophotometer.

Calcium, K, Mg, and P were analyzed by the International Minerals and Chemical Corporation plant analysis laboratory using emission spectrographic analysis procedures.

Soil Analytical Methods

Surface (0 to 10 cm) soil was collected from the Michigan State University Muck Experimental Farm. A uniform sample was prepared by sieving the soil through a 6-mesh stainless steel screen and mixing thoroughly. Soil moisture content (65%) was determined by the Michigan Cooperative Extension Soil Testing Lab. This was the normal field moisture content and was maintained from time of soil collection throughout the experimental period. A chemical analysis of this soil as adapted from the dissertation of Brown (1949) and Timm (1952) is given in Table 1.

Soil pH

Soil pH was determined by mixing 5 grams of soil with 10 ml of water (1:2 ratio). The mixture was remixed again after 15 minutes and the pH of the suspension read using a Beckman Zeromatic glass electrode pH meter. The soil pH was 6.7. Soil pH was measured on each treatment after cropping and was found to be insignificantly changed with metal addition.

Table 1. Chemical properties of a Houghton muck soil from the Michigan State University Experimental Muck Farm.

pH	6.7
Organic matter, %	82.6
Ash, %	17.4
Exchangeable Hydrogen, meq/100 g	45.1
Total Exchange Capacity, meq/100 g	166.5
Exchangeable Cations, meq/100 g	121.4
Base Saturation, %	72.9
Total N, %	3.3
P, %	0.12
Ca, %	2.5
Mg, %	0.27
Fe, %	1.3
Cu, %	0.0011

Extractable Cadmium, Chromium, Copper, Iron, Manganese, Nickel and Zinc

Soil metals were extracted using three different procedures listed in Table 2. The extractants were used to find the most effective method of determining available soil metals. The metal content in the extract was analyzed by using a Perkin-Elmer Model 303 atomic absorption spectrophotometer.

Table 2. Soil extraction procedures.

Extracting Solution	Soil-Solution Ratio	Method of Extraction	Extraction Time (minutes)
0.1 *N* HCl	5:50	Shaking	30
1.0 *N* NH_4OAc	5:50	Shaking	30
0.005 *M* DTPA	10:40	Shaking	120[a]

[a]Method of Lindsay and Norvell (1969).

Statistical Procedures

All data were subjected to analysis of variance in accordance with a randomized block design. Facilities of Michigan State University Computer Center and STAT routines of the Michigan Agricultural Experiment Station were used.

RESULTS AND DISCUSSION

Effect of Increasing Concentrations of Soil Applied Cadmium upon Growth, Yield, and Nutrient Composition of Corn

Growth and color differences were observed in early stages of plant growth (emergence to 3 weeks). Delayed seedling emergence up to 48 hours compared to the control was caused by the higher rates of Cd (0.25 to 2.0 meq/100 g). Plants receiving the above rates of Cd were stunted and appeared to be somewhat chlorotic in comparison to the control treatment (Plate 1).

Yields of dry matter and plant chemical composition are given in Tables 3 and 4. Soil additions of Cd from 0.25 to 2.0 meq/100 g reduced plant growth (0.69 g/plant to 0.28 g/plant) significantly compared to the control (1.37 g/plant). Increases in Cd concentration from 16 to 136 ppm resulted from soil Cd additions of 0.05 to 2.0 meq/100 g, respectively (Figure 1). Increasing Cd rates reduced plant uptake of Cu, Fe, Mn, and Zn but plant concentration of Cu, Fe, and Zn were not significantly changed due to Cd treatments. These results indicate that uptake of Cu, Fe, and Zn was reduced in proportion to growth reduction due to Cd toxicity. Plant Mn concentration significantly increased at the two highest rates of soil Cd. Addition of Cd to the soil may have displaced some Mn from complexed forms making this metal more available

Plate 1. Photograph showing growth of corn plants grown on Houghton muck after graded additions of cadmium.

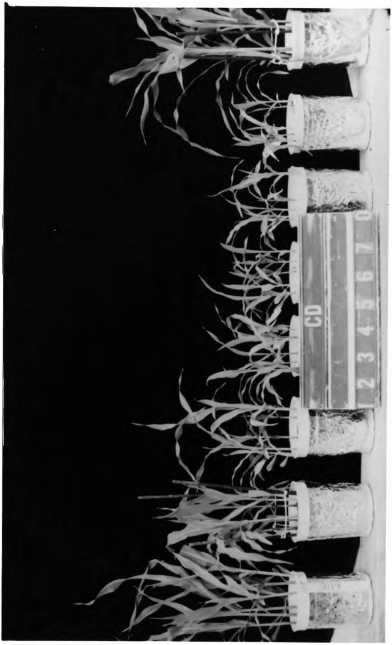

CD

Figure 1. Yields of dry matter and cadmium content of corn plants grown on Houghton muck after graded additions of cadmium.

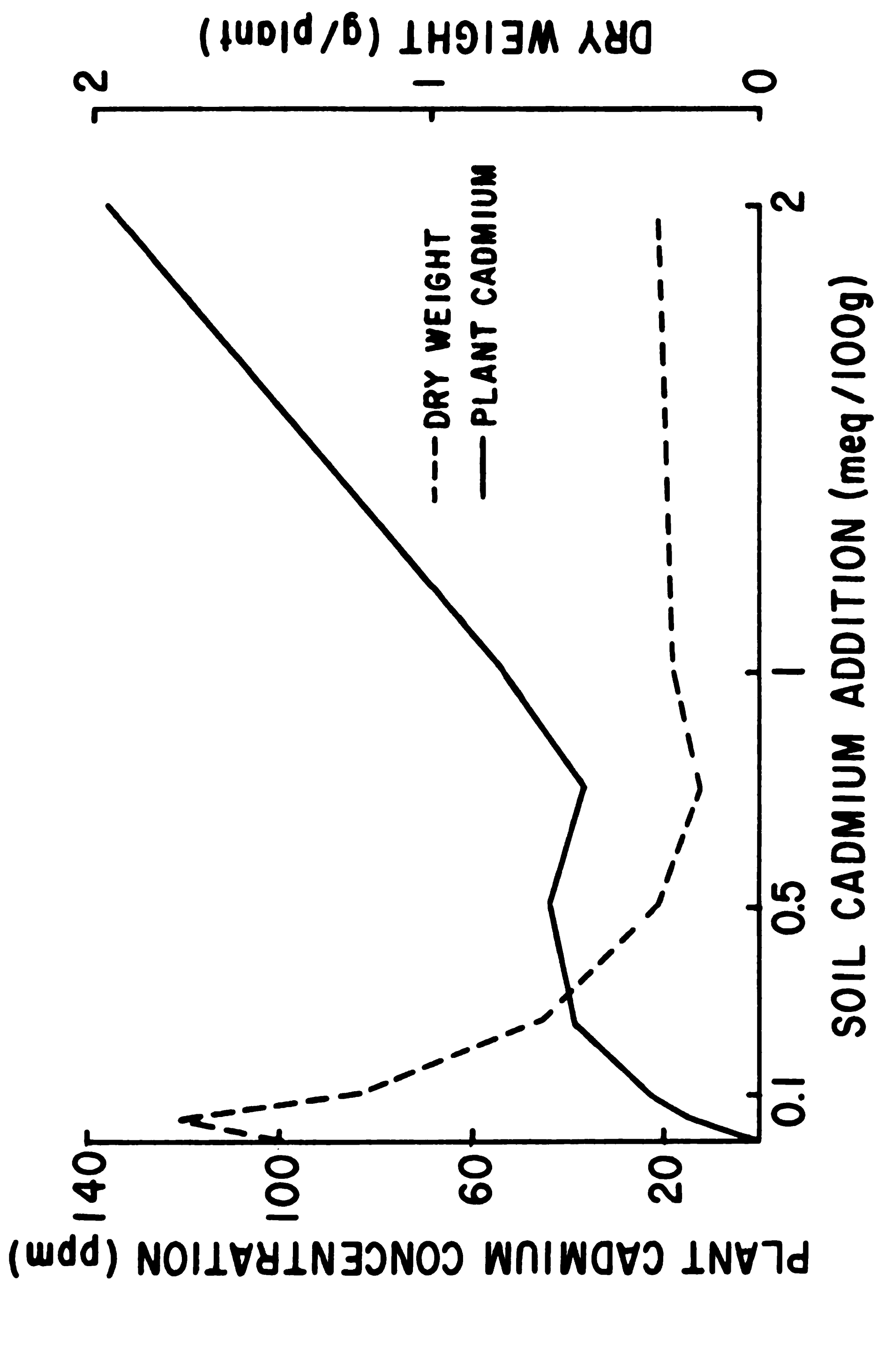

PLANT CADMIUM CONCENTRATION (ppm)
140
100
60
20
0.1
0.5
1
2
SOIL CADMIUM ADDITION (meq/100g)
DRY WEIGHT (g/plant)
0
1
2
---DRY WEIGHT
—PLANT CADMIUM

Table 3. Yields of dry matter and metal content of corn plants grown on Houghton muck after graded additions of cadmium.[a,b]

Cadmium addition		Yield	Cd		Cu		Fe		Mn		Zn	
			conc	uptake	conc	uptake	conc	uptake	conc	uptake	conc	uptake
meq/100 g	ppm	g/plant	ppm	ug/plant	ppm	ug/plant	ppm	ug/plant	ppm	ug/plant	ppm	ug/plant
0	0	1.37	0	0	14	19	141	194	7	10	74	100
0.05	28	1.75	16	28	16	28	125	217	7	12	56	100
0.1	56	1.19	23	27	15	18	94	110	4	4.8	58	69
0.25	140	.69	39	27	19	13	130	89	6	4.3	62	42
0.5	281	.33	44	15	20	7	135	45	7	2.2	83	27
0.75	420	.21	37	8	18	4	137	29	7	1.6	89	18
1.0	562	.24	54	13	19	4	208	49	9	2.2	112	27
2.0	1124	.28	136	38	24	7	147	41	9	2.6	58	16
LSD (0.05)		0.19	18	7.5	N.S.	8	N.S.	39	1	1.5	N.S.	35

[a]Chromium and Nickel levels were below detection limits.
[b]Each value is the average of 4 replications.

Table 4. Yields of dry matter and nutrient content of corn plants grown on Houghton muck after graded additions of cadmium.[a]

Cadmium addition		Yield	Nutrient			
			P	K	Ca	Mg
meq/100 g	ppm	g/plant	%			
0	0	1.37	0.21	3.72	0.69	0.69
0.05	28	1.75	0.25	6.24	0.45	0.36
0.10	56	1.19	0.26	7.13	0.59	0.39
0.25	140	0.69	0.25	7.60	0.66	0.40
0.50	281	0.33	0.25	7.71	0.74	0.42
0.75	420	0.21	0.29	6.33	0.80	0.42
1.00	562	0.24	0.29	7.37	0.86	0.46
2.00	1124	0.28	0.26	7.15	1.29	0.45
LSD (0.05)		0.19	0.03	0.96	0.09	0.04

[a]Each value represents the average of 4 replications.

to the plant. Cadmium additions significantly increased the P and K content of the plants but Mg content was significantly lower in comparison to the control. Calcium content of plants was increased by rates of Cd ranging form 0.75 to 2.0 meq/100 g. Apparently the plants continued to take up P, K, and Ca even when they ceased growing.

Influence of Increasing Soil Cadmium Concentrations upon Soil Extractable Metal Concentrations

Soil extraction data for Cd (Table 5) reveal that 0.1 *N* HCl and 0.005 *M* DTPA removed nearly equal amounts of Cd. Quantities of Cd extracted with 0.1 *N* HCl and 0.005 *M* DTPA ranged from 19 to 871 ppm and 28 to 752 ppm, respectively. Soil extraction with 1 *N* NH_4OAc removed only 20 to 30 percent as much Cd as other extractants. All extractants removed increasing amounts of Cd corresponding to the graded additions of soil Cd. The 0.1 *N* HCl, 0.005 *M* DTPA, and 1 *N* NH_4OAc extracts removed 77, 67, and 19 percent respectively of the added Cd at the 2.0 meq/100 g rate. These data indicate Cd is not fixed strongly by soil particles resulting in availability to plants. Iron and Cu in the 0.1 *N* HCl extract were significantly increased by Cd additions in comparison to the control but the 0.005 *M* DTPA extractable Fe was significantly lower than the control at the high rates of Cd. Manganese and Zn were not significantly influenced by increasing Cd rates.

Table 5. Extraction behavior of selected metals in Houghton muck after graded additions of cadmium followed by cropping with corn.[a,b]

Cadmium addition		Metals and extracting solutions								
		Cd			Cu			Fe		
		0.1 N HCl	0.005 M DTPA	1 N NH_4OAc	0.1 N HCl	0.005 M DTPA	1 N NH_4OAc	0.1 N HCl	0.005 M DTPA	1 N NH_4OAc
meq/100 g	ppm	ppm								
0	0	---	---	---	0.8	4.2	---	24.8	313.5	1.6
0.05	28	19.1	27.7	3.6	0.9	4.6	---	23.0	282.2	1.6
0.10	56	41.7	45.2	8.1	0.9	5.2	---	25.6	293.2	1.7
0.25	140	101.8	95.8	24.2	1.0	4.9	---	31.1	297.6	1.8
0.50	281	196.5	206.6	55.8	1.6	4.4	---	37.4	239.9	2.0
0.75	420	324.3	335.7	84.8	1.7	4.1	---	37.9	228.7	2.0
1.00	562	463.0	394.4	125.1	1.8	4.0	---	42.7	222.2	2.3
2.00	1124	870.7	752.2	216.6	1.3	3.5	---	33.6	236.7	1.8
LSD (0.05)		19.1	14.1	14.7	0.2	0.9	N.S.	9.5	57.6	0.3

Table 5 (continued)

Cadmium addition		Metals and extracting solutions					
		Mn			Zn		
		0.1 N HCl	0.005 M DTPA	1 N NH_4OAc	0.1 N HCl	0.005 M DTPA	1 N NH_4OAc
meq/100 g	ppm	ppm					
0	0	21.9	1.1	0.1	14.0	8.6	0.8
0.05	28	29.1	1.6	0.2	9.7	7.0	0.9
0.10	56	32.1	1.5	0.2	10.6	7.2	1.0
0.25	140	30.8	1.4	0.1	18.8	7.4	0.8
0.50	281	37.3	1.0	0.2	9.9	9.9	2.6
0.75	420	35.3	0.7	0.0	8.4	6.9	1.8
1.00	562	37.2	0.9	0.2	8.9	11.4	2.1
2.00	1124	30.2	1.7	0.8	17.9	7.6	3.4
LSD (0.05)		N.S.	N.S.	0.3	N.S.	N.S.	N.S.

[a]Each value represents the average of 4 replications.
[b]Chromium and Nickel levels were below detection limits.

Effect of Increasing Concentrations of Soil Applied Chromium upon Plant Growth, Yield, and Nutrient Composition of Corn

Growth differences due to Cr treatments were significantly different from the control (Plate 2). Plant dry weight yields increased significantly in all Cr treatments when compared to the control. Dry weights ranging from 1.37 g/plant in the control to 2.71 g/plant at the 1.0 meq/100 g Cr rate indicate a doubling of the dry weight yield due to the Cr treatment. Visual growth differences between the control plants and the plants grown on the Cr amended soil other than plant size were not evident. A chemical analysis of plant material is presented in Tables 6 and 7. Detectable levels of Cr were not translocated to the plant tops. Concentrations of Cr, Fe, and Zn in plant tissue due to Cr treatment were not significantly different from the control. Plant Mn uptake was significantly increased due to increasing Cr rates (Figure 2). Manganese uptake increased from 9 ug/plant in the control to 49 ug/plant with the 2.0 meq/100 g rate of Cr. The increase in plant growth probably resulted from a displacement of Mn from the soil complex by the added Cr with a subsequent increase in available Mn for plant uptake. Chromium treatments increased plant K concentration while decreasing Mg and Ca concentrations significantly. Phosphorus content in plant tops was increased with Cr rates up to 0.25 meq/100 g but higher Cr rates significantly decreased the plant P concentration.

Plate 2. Photograph showing growth of corn plants grown on Houghton muck after graded additions of chromium.

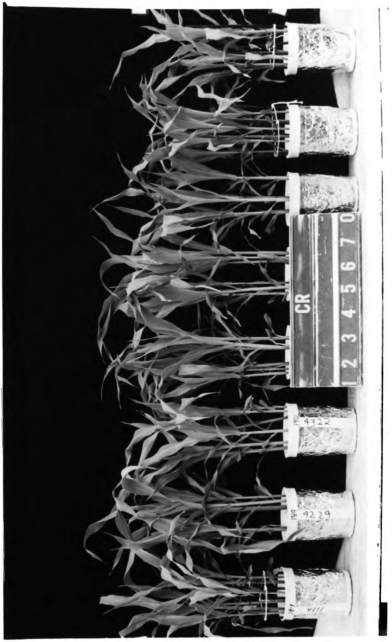

CR
4322
4229

Figure 2. Yields of dry matter and manganese uptake of corn plants grown on Houghton muck after graded additions of chromium.

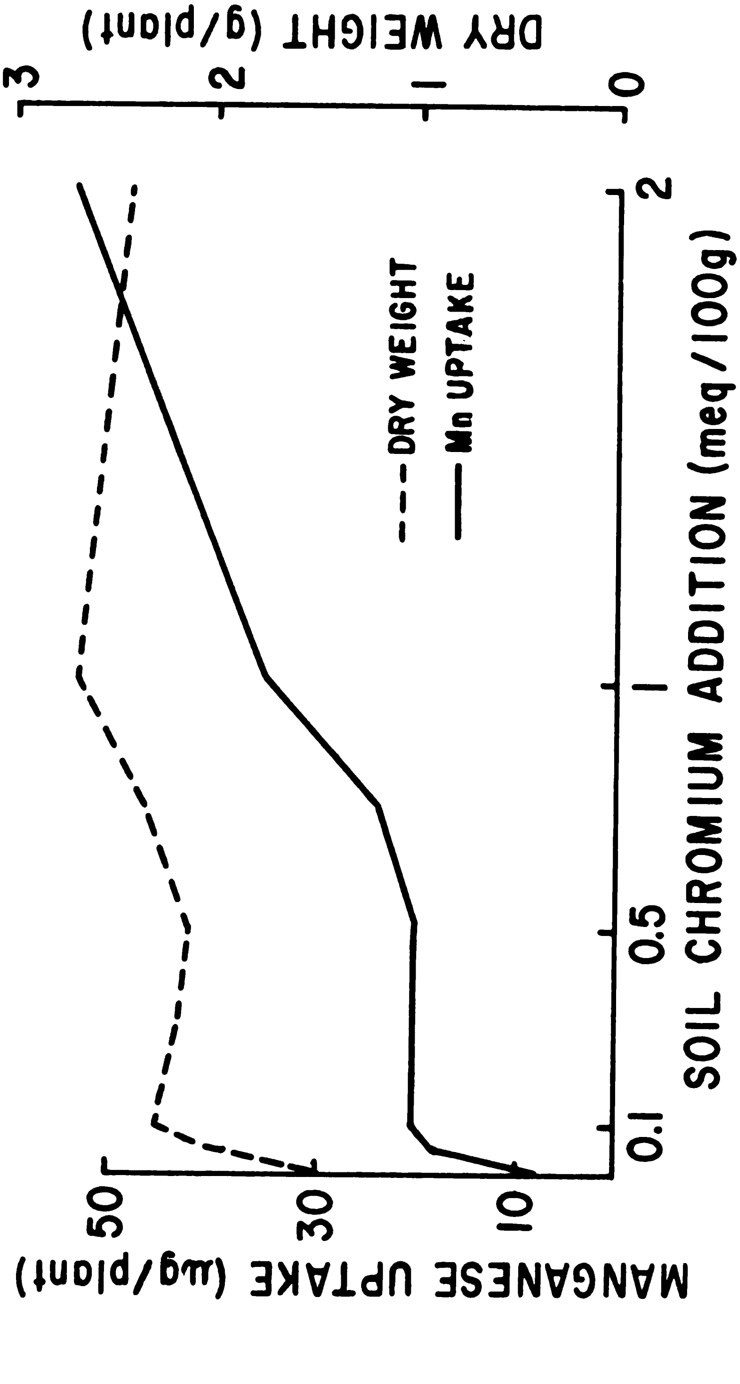

MANGANESE UPTAKE (µg/plant)
50
30
10
DRY WEIGHT (g/plant)
3
2
1
0
SOIL CHROMIUM ADDITION (meq/100g)
0.1
0.5
1
2
DRY WEIGHT
Mn UPTAKE

Table 6. Yields of dry matter and metal content of corn plants grown on Houghton muck after graded additions of chromium.[a,b]

Chromium addition		Yield	Cu		Fe		Mn		Zn	
			conc	uptake	conc	uptake	conc	uptake	conc	uptake
meq/100 g	ppm	g/plants	ppm	ug/plant	ppm	ug/plant	ppm	ug/plant	ppm	ug/plant
0	0	1.37	14	19	141	194	7	4	74	99
.05	9	2.06	17	35	125	259	9	18	63	131
.10	17	2.27	18	41	163	371	9	20	73	168
.25	43	2.23	20	43	121	269	9	20	57	126
.50	87	2.20	13	28	129	284	9	20	56	125
.75	130	2.32	13	31	129	394	10	24	66	146
1.0	173	2.71	15	41	91	251	13	35	63	166
2.0	347	2.41	17	42	149	352	20	49	85	198
LSD (0.05)		.39	N.S.	13	N.S.	101	2.0	8	N.S.	N.S.

[a]Cadmium, Chromium, and Nickel levels were non-detectable.
[b]Each value represents the average of 4 replications.

Table 7. Yields of dry matter and nutrient content of corn plants grown on Houghton muck after graded additions of chromium.[a]

Chromium addition		Yield	Nutrient			
			P	K	Ca	Mg
meq/100 g	ppm	g/plant	%			
0	0	1.37	.21	3.72	.69	.69
0.05	9	2.06	.24	5.98	.45	.39
0.10	17	2.27	.26	5.62	.44	.37
0.25	43	2.23	.24	5.70	.44	.38
0.50	87	2.20	.19	5.39	.45	.38
0.75	130	2.32	.19	5.43	.46	.38
1.0	173	2.70	.19	4.58	.48	.36
2.0	347	2.41	.17	5.24	.53	.38
LSD (0.05)		.39	.02	1.10	.05	.04

[a]Each value represents the average of 4 replications.

Influence of Increasing Soil Chromium Concentrations upon Soil Extractable Metal Concentrations

Results of metal extraction of soils receiving graded additions of Cr are given in Table 8. Two of the extracting solutions (0.005 M DTPA and 1 N NH_4OAc) did not remove any detectable Cr from the soil. The 0.1 N HCl extracting solution removed only small amounts of Cr ranging from 0.1 to 2.3 ppm. Soil Cr additions significantly decreased the 0.1 N HCl and 0.005 M DTPA extractable Fe below the control treatment. These data indicate the Cr is very tightly bound by the soil complex, possibly by soil organic matter or by complexing with soil Fe. Extractable Cu, Mn, and Zn were not significantly affected by graded Cr additions.

Effect of Increasing Concentrations of Soil Applied Nickel upon Plant Growth, Yield, and Nutrient Composition of Corn

Plants grown on soil receiving rates of Ni from 0.1 to 3.0 meq/100 g increased in dry weight while rates of Ni above 3.0 meq/100 g caused a significant dry weight reduction. Foliage color of plants growing on soil receiving rates up to 3.0 meq/100 g was similar to the control but higher rates of Ni caused interveinal chlorosis (6.0 meq/100 g) and plant death (9.0 meq/100 g). Plants grown on soil treated with 9.0 meq/100 g became very light in color within 3 weeks and turning brown at 5 weeks (Plate 3). A chemical analysis of the plant tissue is given in Tables 9 and 10. Nickel concentration in plant tops was increased significantly corresponding to soil Ni additions (Figure 3). The Ni content in plant tissue ranged from 6 to 508 ppm. Nickel became toxic

Plate 3. Photograph showing growth of corn plants grown on Houghton muck after graded additions of nickel.

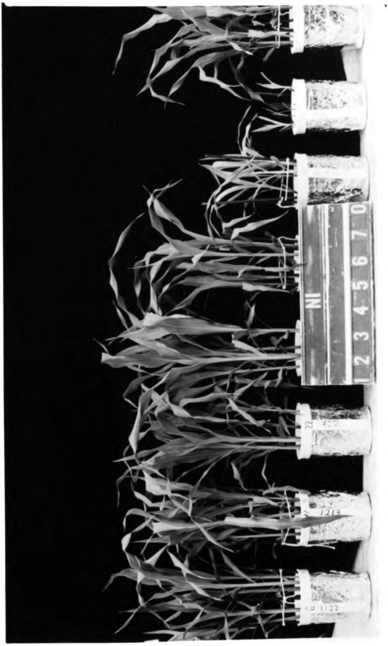


Figure 3. Yields of dry matter and nickel content of corn plants grown on Houghton muck after graded additions of nickel.

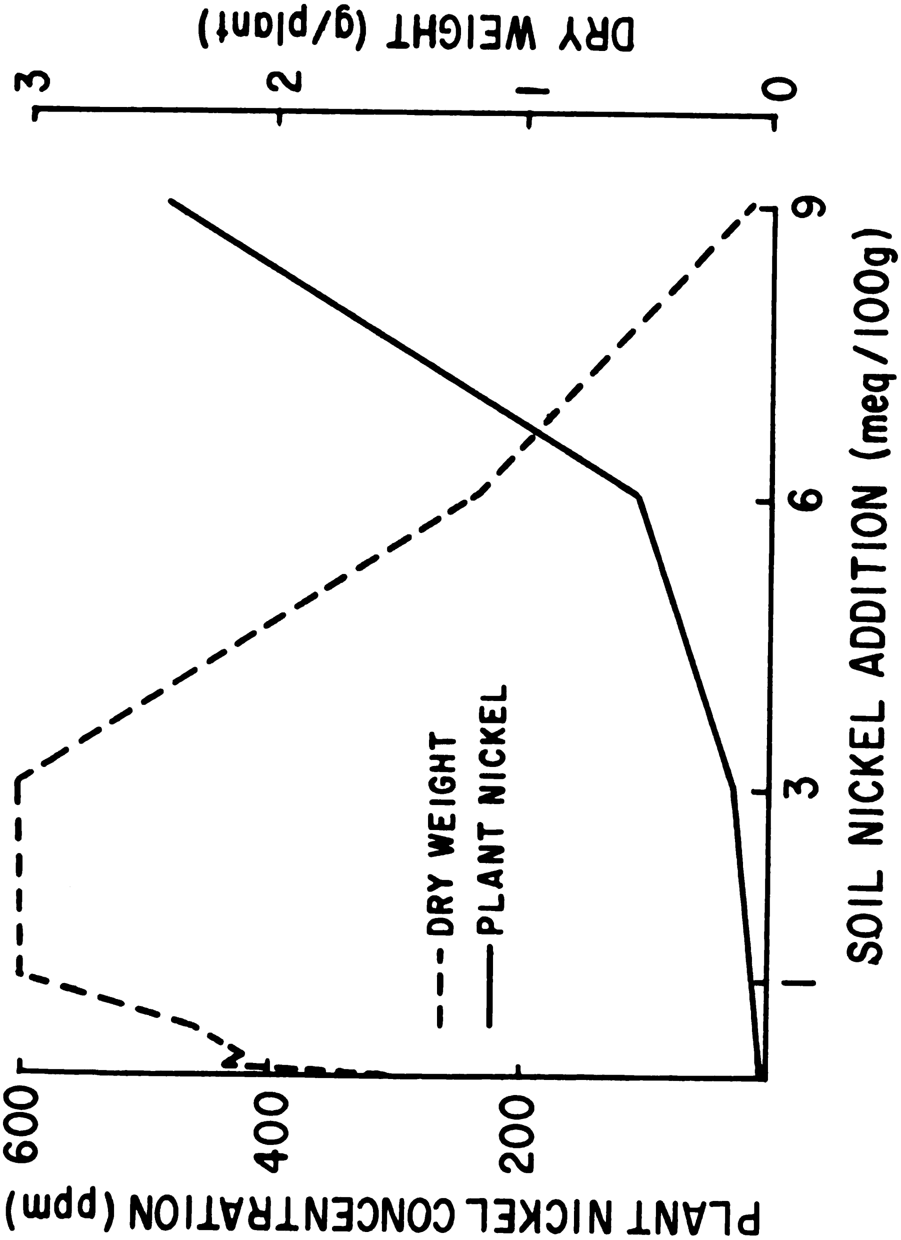

PLANT NICKEL CONCENTRATION (ppm)
600
400
200
DRY WEIGHT (g/plant)
3
2
1
0
SOIL NICKEL ADDITION (meq/100g)
1
3
6
9
DRY WEIGHT
PLANT NICKEL

Table 8. Extraction behavior of selected metals in Houghton muck after graded additions of chromium followed by cropping with corn.[a,b]

Chromium addition		Metals and extracting solutions								
		Cr			Cu			Fe		
		0.1 N HCl	0.005 M DTPA	1 N NH_4OAc	0.1 N HCl	0.005 M DTPA	1 N NH_4OAc	0.1 N HCl	0.005 M DTPA	1 N NH_4OAc
meq/100 g	ppm	ppm								
0	0	---	---	---	0.8	4.2	---	24.8	313.5	1.5
0.05	9	---	---	---	0.7	4.4	---	19.1	281.0	1.4
0.10	17	0.1	---	---	0.7	4.5	---	17.6	293.6	1.2
0.25	43	0.4	---	---	0.6	4.6	---	17.5	287.7	1.2
0.50	87	0.6	---	---	0.6	4.4	---	16.7	266.4	1.4
0.75	130	1.0	---	---	0.5	4.7	---	15.2	276.0	1.3
1.00	173	1.3	---	---	0.5	4.6	---	15.1	282.0	1.0
2.00	347	2.3	---	---	0.5	4.5	---	16.4	285.3	1.4
LSD (0.05)		0.2			0.1	N.S.		5.0	20.7	N.S.

Table 8 (continued)

Chromium addition		Metals and extracting solutions					
		Mn			Zn		
		0.1 N HCl	0.005 M DTPA	1 N NH_4OAc	0.1 N HCl	0.005 M DTPA	1 N NH_4OAc
meq/100 g	ppm	ppm					
0	0	21.9	1.1	0.1	14.0	8.6	1.7
0.05	28	19.0	1.2	---	17.8	8.0	0.7
0.10	56	20.9	1.4	0.2	9.0	11.4	1.1
0.25	140	20.5	1.4	0.2	8.3	14.8	0.4
0.50	281	21.5	1.2	0.2	7.4	11.0	1.6
0.75	420	20.1	1.4	0.2	9.1	9.2	1.1
1.00	562	16.4	1.4	0.2	7.1	6.9	0.8
2.00	1124	20.4	1.4	0.3	7.7	10.1	1.1
LSD (0.05)		N.S.	N.S.	N.S.	N.S.	N.S.	N.S.

[a]Each value represents the average of 4 replications.
[b]Cadmium and Nickel levels were below detection limits.

Table 9. Yields of dry matter and metal content of corn plants grown on Houghton muck after graded additions of nickel.[a,b]

Nickel addition		Yield	Ni		Cu		Fe		Mn		Zn	
			conc	uptake	conc	uptake	conc	uptake	conc	uptake	conc	uptake
meq/100 g	ppm	g/plant	ppm	ug/plant	ppm	ug/plant	ppm	ug/plant	ppm	ug/plant	ppm	ug/plant
0	0	1.37	---	---	14	19	141	194	7	9	74	100
0.1	29	2.17	7	15	16	35	124	272	9	19	47	101
0.2	59	2.10	6	13	15	33	144	303	9	19	67	137
0.5	147	2.30	9	21	12	28	96	217	6	13	58	132
1.0	293	3.01	12	38	16	48	100	304	9	26	51	153
3.0	880	3.02	24	72	13	42	108	324	16	47	69	208
6.0	1761	1.19	89	102	12	14	99	119	23	28	46	59
9.0	2641	0.09	508	49	11	1	91	9	26	2	74	7
LSD (0.05)		.49	11	27	3	9	35	100	4	12	N.S.	50

[a]Cadmium and Chromium levels were non-detectable
[b]Each value represents the average of 4 replications.

Table 10. Yields of dry matter and nutrient content of corn plants grown on Houghton muck after graded additions of nickel.[a]

Nickel addition		Yield	Nutrient			
			P	K	Ca	Mg
meq/100 g	ppm	g/plant	%			
0	0	1.37	.21	3.71	.69	.69
0.1	29	2.17	.23	5.62	.42	.34
0.2	59	2.10	.26	5.88	.42	.36
0.5	147	2.30	.24	5.13	.44	.38
1.0	293	3.01	.23	4.19	.45	.36
3.0	880	3.02	.25	3.96	.63	.42
6.0	1761	1.19	.19	5.25	1.35	.49
9.0	2641	0.09	.20	3.46	3.44	.80
LSD (0.05)		.49	.02	.59	.17	.06

[a]Each value represents the average of 4 replications.

to the plants when the concentration in the plant was greater than 24 ppm as indicated by reduced plant dry weight and visual toxic symptoms. Increases in yield of plant dry weight at lower rates of Ni (0.1 to 3.0 meq/100 g) was probably due to a displacement of adsorbed or complexed Mn and Cu with a subsequent increase in Mn and Cu uptake (Figures 4 and 5). Plant uptake of Mn and Cu is significantly increased above the control with increasing soil Ni treatments up to 3.0 meq/100 g but higher treatments reduced uptake of Mn and Cu. Plant Fe concentration was reduced significantly below the control with added Ni. Reduced plant Fe concentration may cause a more favorable Fe/Mn ratio in the plant resulting in increased Mn uptake. Plants which were slightly Mn deficient may have responded to this increase in Mn uptake by increased growth (plant dry weight). There was no significant difference in plant Zn concentration with increasing Ni rates. Plant concentration of P, K, and Mg were not significantly different from the control. The plant Ca concentration was significantly increased at the 6.0 and 9.0 meq/100 g addition of Ni.

<u>Influence of Increasing Soil Nickel Concentrations upon Soil Extractable Metal Concentrations</u>

Results from the soil extractions (Table 11) indicate that 1 N NH_4OAc removed only a small amount of the added Ni. The 0.1 N HCl removed between 36 and 102 percent as much Ni as did the 0.005 M DTPA solution. Each extracting solution removed increasing amounts of Ni corresponding to added soil

Figure 4. Yields of dry matter and copper uptake of corn plants grown on Houghton muck after graded additions of nickel.

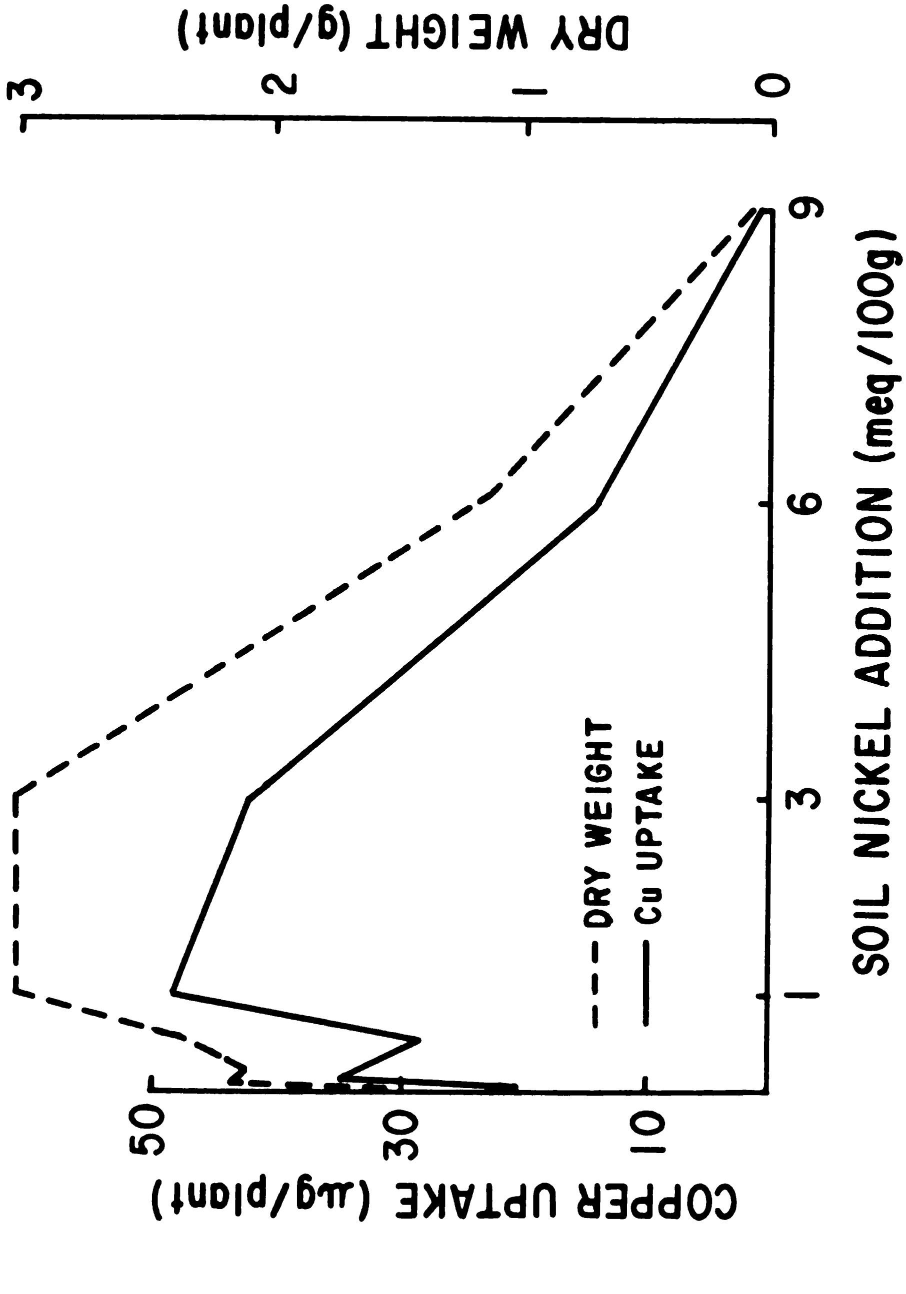

DRY WEIGHT (g/plant)
3
2
1
0
COPPER UPTAKE (µg/plant)
50
30
10
1
3
6
9
SOIL NICKEL ADDITION (meq/100g)
DRY WEIGHT
Cu UPTAKE

Figure 5. Yields of dry matter and manganese uptake of corn plants grown on Houghton muck after graded additions of nickel.

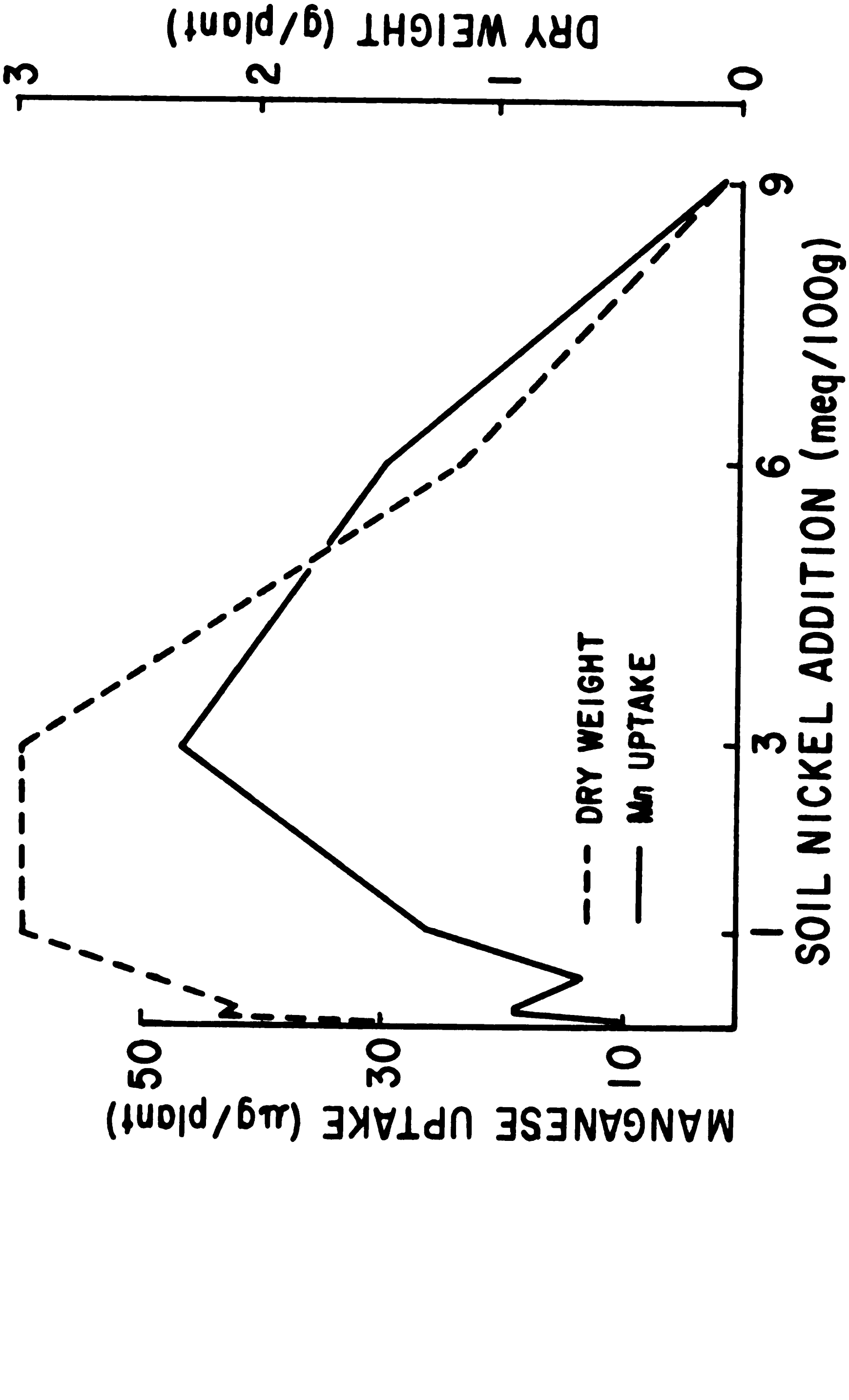

DRY WEIGHT (g/plant)
0
1
2
3
MANGANESE UPTAKE (µg/plant)
10
30
50
SOIL NICKEL ADDITION (meq/100g)
1
3
6
9
DRY WEIGHT
Mn UPTAKE

Table 11. Extraction behavior of selected metals in Houghton muck after graded additions of nickel followed by cropping with corn.[a,b]

Nickel addition		Metals and extracting solutions								
		Ni			Cu			Fe		
		0.1 N HCl	0.005 M DTPA	1 N NH_4OAc	0.1 N HCl	0.005 M DTPA	1 N NH_4OAc	0.1 N HCl	0.005 M DTPA	1 N NH_4OAc
meq/100 g	ppm	ppm								
0	0	---	---	---	0.8	4.3	---	24.8	313	1.6
0.1	29	6.4	17.7	---	0.6	4.7	---	16.6	257	1.5
0.2	59	13.7	29.5	---	0.8	4.4	---	20.1	257	1.5
0.5	147	46.3	97.4	3.6	0.8	4.7	---	21.5	257	1.6
1.0	293	227.4	236.5	5.8	0.6	4.6	---	13.1	221	1.3
3.0	880	284.9	710.1	38.0	0.7	4.0	---	14.8	131	1.3
6.0	1761	964.0	1273.8	141.8	1.7	1.4	---	31.5	38	1.7
9.0	2641	1628.3	1595.2	245.4	2.7	0.3	---	43.4	31	1.9
LSD (0.05)		170.8	29.4	11.4	0.3	0.5		5.9	26	0.2

Table 11 (continued)

Nickel addition		Metals and extracting solutions					
		Mn			Zn		
		0.1 N HCl	0.005 M DTPA	1 N NH_4OAc	0.1 N HCl	0.005 M DTPA	1 N NH_4OAc
meq/100 g	ppm	ppm					
0	0	21.9	1.2	0.1	14.0	8.6	1.7
0.1	29	16.8	1.2	0.0	11.7	9.5	0.7
0.2	59	21.3	1.3	0.2	8.8	10.0	1.1
0.5	147	24.3	1.5	0.2	10.0	9.2	0.4
1.0	193	16.6	1.1	0.2	5.9	12.1	1.6
3.0	880	16.6	1.1	0.2	11.6	6.1	1.1
6.0	1761	29.6	0.6	0.2	9.8	12.1	0.8
9.0	2641	32.6	0.4	0.3	11.3	5.5	1.1
LSD (0.05)		6.8	0.3	N.S.	N.S.	N.S.	N.S.

[a]Each value represents the average of 4 replications.
[b]Cadmium and Chromium levels were below detection limits.

Ni. There was no significant difference in the amount of Cu extracted due to the soil Ni treatments. The DTPA extractable Mn and Zn was not significantly different from the control levels but DTPA extractable Fe was significantly decreased with added soil Ni. Levels of Cd and Cr were below the detection limits of the atomic absorption spectrophotometer.

Effect of Increasing Concentrations of Soil Applied Zinc upon Growth, Yield, and Nutrient Composition of Corn

Growth increases due to Zn treatments were significant with only two treatments (3.0 and 6.0 meq/100 g). Size and foliage color of plants grown on all Zn treatments were no different than the control (Plate 4). A chemical analysis of the plants is given in Tables 12 and 13. The concentration of Zn in plant tissue ranged from 74 ppm in the control to 1763 ppm with the 9.0 meq/100 g rate of Zn (Figure 6). The applied Zn was not absorbed or complexed by the soil in a form not available to the plants since high amounts of Zn were found in the plant tissue. Additions of Zn increased plant Cu concentrations. The Cu uptake seemed to be related to the plant dry weight increases (Figure 7). Manganese concentration and uptake was increased with the three highest Zn rates. Plant Fe content was not significantly influenced by Zn additions. Phosphorus and K content increased significantly in plant tissue over the control. Calcium content decreased with lower Zn additions (0.1 to 0.5 meq/100 g) but increased with the 9.0 meq/100 g Zn application. Plant Mg

Plate 4. Photograph showing growth of corn plants grown on Houghton muck after graded additions of zinc.


ZN

Figure 6. Yields of dry matter and zinc content of corn plants grown on Houghton muck after graded additions of zinc.

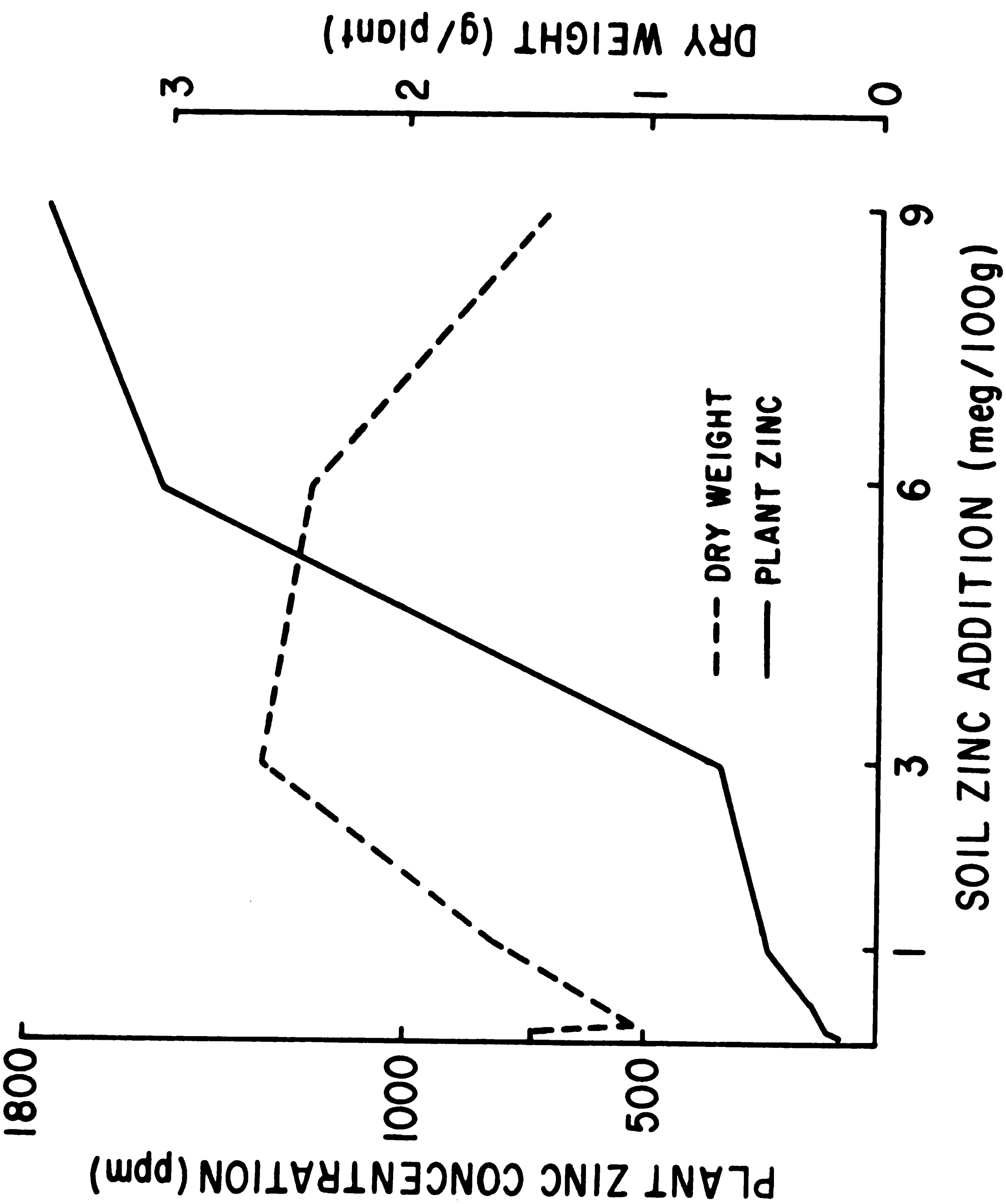
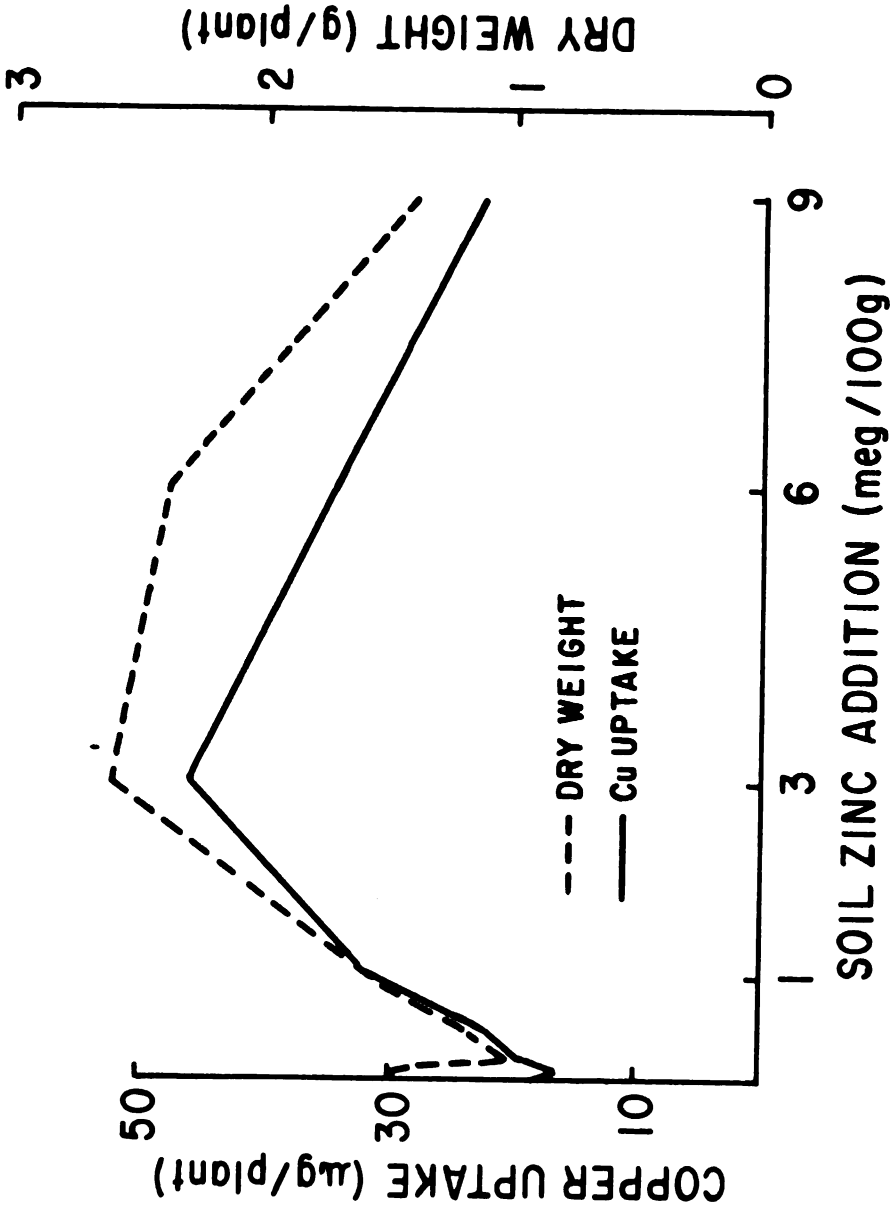

DRY WEIGHT (g/plant)
3
2
1
0
DRY WEIGHT
PLANT ZINC
SOIL ZINC ADDITION (meg/100g)
1
3
6
9
PLANT ZINC CONCENTRATION (ppm)
1800
1000
500

Figure 7. Yields of dry matter and copper uptake of corn plants grown on Houghton muck after graded additions of zinc.



COPPER UPTAKE (µg/plant)
50
30
10
DRY WEIGHT (g/plant)
3
2
1
0
SOIL ZINC ADDITION (meg/100g)
1
3
6
9
DRY WEIGHT
Cu UPTAKE

Table 12. Yields of dry matter and metal content of corn plants grown on Houghton muck after graded additions of zinc.[a,b]

Zinc additions		Yield	Zn		Cu		Fe		Mn	
			conc	uptake	conc	uptake	conc	uptake	conc	uptake
meq/100 g	ppm	g/plant	ppm	ug/plant	ppm	ug/plant	ppm	ug/plant	ppm	ug/plant
0	0	1.37	74	100	14	19	141	194	7	9
0.1	33	1.37	83	113	12	16	101	131	5	6
0.2	65	1.04	113	155	14	19	121	165	5	7
0.5	163	1.32	147	196	17	22	141	188	7	9
1.0	327	1.55	225	349	20	31	136	211	7	10
3.0	980	2.60	335	869	18	46	102	266	13	34
6.0	1961	2.33	1529	3637	15	35	139	330	23	54
9.0	2942	1.42	1763	2535	17	23	141	206	36	49
LSD (0.05)		.45	409	114	N.S.	9	N.S.	90	3	9

[a]Cadmium, Chromium, and Nickel levels were non-detectable.
[b]Each value represents the average of 4 replications.

Table 13. Yields of dry matter and nutrient content of corn plants grown on Houghton muck after graded additions of zinc.[a]

Zinc addition		Yield	Nutrient			
			P	K	Ca	Mg
meq/100 g	ppm	g/plant	%			
0	0	1.37	.21	3.71	.69	.69
0.1	33	1.37	.33	8.7	.47	.41
0.2	65	1.04	.33	8.5	.47	.33
0.5	163	1.32	.30	8.2	.54	.44
1.0	327	1.55	.28	7.5	.61	.47
3.0	980	2.60	.23	5.2	.61	.38
6.0	1961	2.33	.23	5.9	.92	.40
9.0	2942	1.42	.21	6.9	1.39	.47
LSD (0.05)		.45	.04	1.4	.11	.05

[a]Each value represents the average of 4 replications.

content was significantly lower than the control on all treatments of Zn.

Influence of Increasing Soil Zinc Concentration upon Soil Extractable Metal Concentrations

The results of soil extractions are given in Table 14. Amounts of extractable Zn ranged from 14 to 2068 ppm, 9 to 876 ppm, and 1 to 880 ppm with 0.1 N HCl, 0.005 M DTPA, and 1 N NH_4OAc extracting solutions, respectively. These data reveal that most of the added Zn was still in a rather soluble form while the plants were growing. Extractable Cu, Fe, and Mn was not significantly affected by Zn additions.

Table 14. Extraction behavior of selected metals in Houghton muck after graded additions of zinc followed by cropping with corn.[a,b]

Zinc addition		Metals and extracting solutions					
		Zn			Cu		
		0.1 N HCl	0.005 M DTPA	1 N NH_4OAc	0.1 N HCl	0.005 M DTPA	1 N NH_4OAc
meq/100 g	ppm	ppm					
0	0	14	9	1	0.8	4.3	---
0.1	33	27	26	2	0.9	4.5	---
0.2	65	38	38	3	0.8	3.3	---
0.5	163	122	106	13	0.9	4.2	---
1.0	327	241	230	25	1.0	4.3	---
3.0	980	611	671	139	0.6	2.3	0.1
6.0	1961	1327	825	475	1.0	0.4	---
9.0	2942	2068	876	880	1.0	0.3	---
LSD (0.05)		87	60	130	N.S.	1.3	N.S.

Table 14 (continued)

Zinc addition		Metals and extracting solutions					
		Fe			Mn		
		0.1 N HCl	0.005 M DTPA	1 N NH_4OAc	0.1 N HCl	0.005 M DTPA	1 N NH_4OAc
meq/100 g	ppm	ppm					
0	0	25	313	1.5	22	1.2	0.1
0.1	33	26	315	1.2	23	1.6	0.1
0.2	65	23	224	1.3	20	0.9	---
0.5	163	27	281	1.6	29	1.5	0.2
1.0	327	24	286	1.6	22	1.3	0.3
3.0	980	14	66	1.3	16	1.0	0.7
6.0	1961	22	24	1.6	29	0.5	1.4
9.0	2942	24	20	1.6	31	0.6	4.1
LSD (0.05)		N.S.	85	N.S.	N.S.	0.6	0.4

[a]Cadmium, Chromium, and Nickel levels were below detection limits.
[b]Each value represents the average of 4 replications.

SUMMARY AND CONCLUSIONS

Plant growth and heavy metal accumulation was influenced quite differently by Cd, Cr, Ni, and Zn. The addition of Cd resulted in delayed seedling emergence, stunting of plants, and yield reduction. Plant Cd concentration increased from 16 to 136 ppm at levels of 0.05 and 2.0 meq/100 g respectively, indicating that Cd was readily available for plant uptake. Plants grown on Cr treated soils yielded significantly higher in dry weight compared to the control. A resultant chemical analysis of plant tissue showed no detectable Cr, however, a significant increase in Mn uptake was noted (9 to 49 ug per plant). The increase in plant growth may be due to a displacement of Mn from the soil complex with a resultant increase in available Mn for plant uptake. Soil chemical analysis revealed no increase in extractable Mn due to Cr treatments, however, extractable Fe was significantly decreased due to increasing Cr treatments. This may be a possible explanation of increased Mn uptake since soil Fe/Mn ratios affect plant Mn uptake. Soil applied Ni at rates of 1.0 to 3.0 meq/100 g increased plant growth significantly over the control. Rates of Ni above 3.0 meq/100 g reduced plant growth significantly indicating a probable Ni toxicity. Foliage color of plants receiving rates of Ni up to 3.0 meq/

100 g was no different than the control. Plants grown on soils receiving Ni treatments higher than 3.0 meq/100 g were different with interveinal chlorosis at the 6.0 meq/100 g rate and a browning of the leaves and eventual death of the plant at the 9.0 meq/100 g Ni addition. Plant Ni concentrations were increased significantly over the control. When levels of Ni in plant tissue rose above 24 ppm the dry weight was decreased significantly due to Ni toxicity. The increase in growth at the lower levels of soil Ni may be due to a displacement of Mn or Cu with a subsequent increase in Mn and Cu uptake similar to the phenomenon with the Cr treatments. Soil analysis revealed that DTPA extractable Fe decreased with increasing Ni rates. Soil Zn treatments increased growth at two rates (3.0 and 6.0 meq/100 g). Plant size and foliage color with all Zn treatments were similar to the control. Chemical analysis of plant tissue revealed increasing concentrations of Zn with corresponding increasing Zn treatments (74 to 1763 ppm at the 0 and 9.0 meq/100 g rates). The high Zn accumulations in plant tissue indicate that applied Zn was readily available for plant uptake. Copper uptake increased or decreased with increasing or decreasing plant growth, indicating Cu was not influenced by Zn treatments.

The soil extractants varied greatly in their ability to extract metals from the soil. Both 0.1 N HCl and 0.005 M DTPA worked well in extracting heavy metals and were about equal in amounts extracted. 1 N NH_4OAc was less effective than 0.1 N HCl or 0.005 M DTPA in terms of amounts of metals

extracted, however, each extractant removed increasing amounts of metals with increasing metal rates with the exception of the Cr treatments in which only 0.1 N HCl removed Cr. Soil extraction of the metals indicates Cd, Ni, and Zn were in a rather soluble form in the soil while Cr was in a form which was unavailable. Plant chemical analysis generally, if not wholly, agree with this observation. In terms of potential plant toxicity the metals would be arranged in the following order from greatest to least toxic: Cd>Ni>Zn>Cr.

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